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A completely ab-initio investigation of grain boundaries in solids has been performed for the first time. The electronic and structural properties of two short-period twist boundaries in Ge have been explored and found to be extremely complex. Boundary bonds are found to be distorted and weak, three-fold and five- fold coordinated defects appear to exist, and topological disorder in the form of odd and even numbers of rings of bonds is found to prevail. Complete total energy surfaces as a function of displacement of one grain over the other have also been mapped out. The results predict that there is a large degeneracy in the number of local energy minima, that tunneling -like modes should exist in these boundaries, that the formation energies of the boundaries lie in the range between 4 and 7 eV per unit cell, that the boundary volumes involve expansions in the range of 0.1 to 0.3 A/unit area, that trends toward dimerization exist parallel to the boundary planes, that electronic states will exist deep in the fundamental gaps of these systems, and that the electronic grain boundary states are localized to within a couple of atomic layers away from the interface.

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Abstract

A completely ab-initio investigation of grain boundaries in solids has been performed for the first time. The electronic and structural properties of two short-period twist boundaries in Ge have been explored and found to be extremely complex. Boundary bonds are found to be distorted and weak, three-fold and five- fold coordinated defects appear to exist, and topological disorder in the form of odd and even numbers of rings of bonds is found to prevail. Complete total energy surfaces as a function of displacement of one grain over the other have also been mapped out. The results predict that there is a large degeneracy in the number of local energy minima, that tunneling -like modes should exist in these boundaries, that the formation energies of the boundaries lie in the range between 4 and 7 eV per unit cell, that the boundary volumes involve expansions in the range of 0.1 to 0.3 A/unit area, that trends toward dimerization exist parallel to the boundary planes, that electronic states will exist deep in the fundamental gaps of these systems, and that the electronic grain boundary states are localized to within a couple of atomic layers away from the interface.

Progress

Our purpose in this proposal has been tc perform the first ab-initio investigation of the microscopic properties of a grain boundary in a solid. We have succeeded. Using ab-initio pseudopotentials, density functional theory, and a molecular dynamics approach for total energy calculations, we have made an in-depth, systematic, and exhaustive study to predict a variety of electronic, structural, and dynamical properties of two grain boundaries in Ge. The boundaries chosen involve Σ5 and Σ5* (100) twist geometries. These are very complex grain boundaries with many degrees of freedom. Not surprisingly, absolutely nothing was known theoretically or experimentally about these interfaces. Clearly, they represent stringent test cases for an ab-initio theory.

Our quest has been to determine the nature of the low energy geometries of these boundaries, to determine correlations between defects, structural topology, connectivity and the total energy of a geometry, to map out intergranular interaction energies and to relate geometric structure to electronic structure.

Because of the great inherent complexity of these grain boundaries it is impossible to sample the entire multidimensional phase space. Our approach therefore was to make global scans of phase space retaining many degrees of freedom frozen-in but permitting the most important degrees of freedom to vary. This allowed us to zero-in on potential low energy regions of phase space and then release the rest of the degrees of freedom in order to obtain the lowest energy geometries. In each case, the relaxation process involved rapid quenches from a variety of initial conditions. The final quench always involved simultaneous relaxation of electronic, volume, translational and ionic degrees of freedom. This information was then used to construct various intergranular interation energy maps for both Σ5 and Σ5* boundaries.

Many interesting results emerge. There are many metastable minima reminiscent of the glass problem. All the geometries studied have formation energies in the range of 4 to 7 eV. In each case the volume change of the interface is positive, with variations in the range 0.1 to 0.3A. Statistically, the lower energy geometries appear to correlate with the smaller grain boundary widths. Surprisingly, however, there is no direct correlation between bond-

coordination and total energy. Geometries with all atoms in four-fold coordination could have formation energies which are higher than geometries containing bond-coordination defects. The reason for this is the large disorder in bond-lengths and bond-angles present in the former geometries. Typical bond-coordination defects are dangling bond sites and over coordinated atoms. Surprisingly, the presence of four-fold rings of bonds can also be found in many of these geometries.

The number of dimer bond configurations parallel to the interface tend to be higher in S5* than S5 boundaries and appear to be correlated with lower energy geometries. The translation states associated with the low energy geometries have been determined and are different for S5 and S5*.

Another very interesting result is the discovery of tunneling-like mode configurations. Remarkably, these are geometries which are very similar in energy but are inter-related through simple distortions of the atoms that do not require any significant bond breaking. In fact, the distortions are very similar to those of an NH_3 molecule. Such tunnelling modes have only been known previously to exist in glasses.

Finally, a thorough analysis of the electronic states, charge densities and local densities of state in different regions of the interface was performed. The results revealed that all the geometries had similar distributions of states in the gap which were quite localized in the vicinity of the interface. This is true even for the geometries having no bond-coordination defects because of the large strains in bond angles and bond lengths. Thus the S5 and S5* boundaries should be electrically active and a significant reduction in this activity could be accomplished with hydrogen passivation.

Publications

1. M. Payne, P. Bristowe and J.D. Joannopoulos, "Ab-initio Determination of the Structure of a Grain Boundary," Phys. Rev. Lett. **58** 1348 (1987).

2. M. Payne, P. Bristowe and J.D. Joannopoulos, "Theoretical Investigation of Twist Boundaries in Ge," Mat. Res. Soc. **77**,205 (1987).

3. M. Payne, P. Bristowe and J.D. Joannopoulos, " Ab-initio Calculation of the Microscopic Properties of a Grain Boundary in Germanium," Journ. de Phys. **49**, c5-151 (1988).

4. E. Tarnow, P. Bristowe, J.D. Joannopoulos and M. Payne, "Intergranular Total Energy Maps and the Structure of a Grain Boundary," in Polycrystalline Semiconductors, p. 2, Springer Verlad (1989).

5. E. Tarnow, P. Bristowe, J.D. Joannopoulos and M. Payne, "Ab-initio Molecular Dynamics Approach to the Study of Grain Boundaries in Semiconductors,"Mat. Res. Soc. **141**, 333 (1989).

6. E. Tarnow, P. Bristowe, J.D. Joannopoulos and M. Payne, "Predicting the Structure and Energy of a Grain Boundary in Germanium, "J. of Phys. CM **1**, 327 (1989)>

7. E. Tarnow, P. Dallot, P. Bristowe, J.D. Joannopoulos, G. Francis, and M. Payne, "Structural Complexity in Grain Boundaries with Covalent Bonding", submitted to Physical Review (1990).

Invited Talks at Conferences

1. Third Int'l Workshop on "Total Energy and Force Methods," Trieste, Italy (1987)

2. Workshop on "Physical and Mechanical Properties of Alloys,"Dayton, Ohio (1987)

3. Euro. Conf. Semi. Surf., Bologna, Italy (1988)

4. Int. Conf. on Polycrystalline Semiconductors, Malente, Germany (1988)

5. Mat. Res. Soc. meeting, Boston, Mass. (1988)

6. Workshop on Comp. Algor., Urbana, Illinois (1989)

7. Conf. on Comp. Mod. New. Mat., Bristol, UK (1989)

8. Eighth Int'l Sur Sci. conf., Liverpool, UK (1989)

9. Workshop on Mol. Dyn. Sim, Laguna Beach, CA. (1989)

10. Am. Phys. Soc., Bull 34, 1435 (1989)

11. Workshop on Fracture Computations, Gaithersberg, MD (1989)

12. Mat. Res. Soc. meeting, San Francisco (1990)